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Characterization of Iron (II) Octahedral Complexes with  $\alpha$ -Dioximes and Possibility of Application of  $\alpha$ -Furyldioxime to Chemical Analysis of Iron (II) (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)

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## Characterization of Iron(II) Octahedral Complexes with $\alpha$ -Dioximes and Possibility of Application of $\alpha$ -Furyldioxime to Chemical Analysis of Iron(II)

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$\text{Fe(II) (DgH)}_2\text{X}_2$  and  $\text{Fe(II) (FrH)}_2\text{X}_2$  ( $\text{X}=\text{base}$ ,  $\text{DgH}_2=\text{dimethylglyoxime}$  and  $\text{FrH}_2=\alpha\text{-furyldioxime}$ ) were characterized on the basis of measurements of Mössbauer effect and absorption spectra. These complexes were diamagnetic and exhibited considerably large quadrupole splitting (1.3–1.9 mm/s). There were linear relationships between the charge-transfer band maxima and the basicities of free bases. Marked solvent effects were found in the  $d\pi \rightarrow \pi^*$  (base) charge-transfer bands of  $\text{Fe(II) (DgH)}_2\text{X}_2$ .  $\alpha$ -Furyldioxime was an effective reagent for extraction of ferrous ion in an aqueous solution into chloroform in the presence of bases. The plots of absorbance of the butylamine system at 594 nm *vs.* amount of iron(II) in the range of 1.12–11.2  $\mu\text{g}$  gave a straight line passing through the origin and the molar extinction coefficient estimated from the calibration curve was 19,800  $\text{dm}^3/(\text{mol cm})$ .

KEY WORDS : Iron(II)/  $\alpha$ -Dioximes/ Lewis bases/  
Characterization / Solvent extraction /

Bis(dimethylglyoximate)iron(II),  $\text{Fe(II) (DgH)}_2$ , forms octahedral complex,  $\text{Fe(II) (DgH)}_2\text{X}_2$  ( $\text{X}=\text{base}$ ), with bases such as pyridine and imidazole. In  $\text{Fe(II) (DgH)}_2\text{Im}_2$  ( $\text{Im}=\text{imidazole}$ ), two imidazole molecules coordinate axially as shown in Fig. 1.<sup>1)</sup> While the octahedral complex is stable in solid, it is oxidized by oxygen in the absence of the base and reacts with carbon monoxide through a dissociation mechanism in solution.<sup>2,3)</sup> Therefore, it is thought to be important to study the nature of the bonding between axial ligands and the planar complex in order to understand axial ligand effect on the reactivity of iron(II) complexes with carbon monoxide.

The absorption spectra of  $\text{Fe(II) (DgH)}_2\text{X}_2$  and  $\text{Fe(II) (CdH)}_2\text{X}_2$  ( $\text{X}=\text{pyridine derivatives and CdH}_2=\text{nioxime}$ ) show characteristic charge-transfer (CT) bands in the visible region, which shift markedly due to substituted groups in the pyridine ring.<sup>2,4–7)</sup> The axial ligand effect has been discussed by taking into account the  $\pi$ -interaction between the bases and the central metal ion.<sup>2,6,7)</sup> These complexes exhibit also the CT bands attributed to the  $\pi$ -interaction between the metal ion and the equatorial ligands.<sup>5)</sup> It is known that the quadrupole splitting (Q. S.) of  $\text{Fe(II) }(\alpha\text{-dioxime})_2\text{X}_2$  ( $\text{X}=\text{pyridine and imidazole}$ ), which have a low-spin  $d^6$  electronic configuration, is relatively large.<sup>8,9)</sup> On

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the other hand, the Q. S. values of the complexes containing CO and  $\text{CN}^-$  as axial ligand are normally small.<sup>9)</sup> Therefore, the results also suggest that the axial ligand effect on the Mössbauer parameters may as well be discussed in terms of the  $\pi$ -interaction.

The author reinvestigated the spectroscopic properties of iron(II)- $\alpha$ -dioxime complexes ( $\alpha$ -dioxime=dimethylglyoxime and  $\alpha$ -furyldioxime) through the Mössbauer and the optical absorption measurements prior to study of axial ligand effect on the reactivity of the complexes with carbon monoxide and isocyanides. It was found during this investigation that molar extinction coefficients of the CT bands of  $\alpha$ -furyldioxime complexes are considerably large. Therefore, the author studied possibility of an application of  $\alpha$ -furyldioxime to extraction and determination of iron(II) as well.

### EXPERIMENTAL

Ethanol and the bases except 4-aminopyridine and 4-cyanopyridine were obtained commercially and distilled at ordinary or reduced pressure. Dimethylglyoxime ( $\text{DgH}_2$ ),  $\alpha$ -furyldioxime ( $\text{FrH}_2$ ) and the other reagents were of guaranteed grade and used without further purification. Iron(II)- $\alpha$ -dioxime complexes were prepared under a nitrogen atmosphere according to either of the following procedures: (i) Methanol-water solutions of Mohr's salt and  $\alpha$ -dioxime were mixed and then a base in methanol was added to the mixed solution, and (ii) to an ethanol solution of  $\alpha$ -dioxime,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in an aqueous solution was added and then a base in ethanol was added to the mixed solution. When the 4-cyanopyridine and nicotinic aldehyde complexes were prepared, the pH values of the mixed solutions were adjusted to about 7 by adding an aqueous NaOH solution. The elemental analyses of the isolated complexes are shown in Table I. Iron (II) stock solution (3.92 mg/ml) was prepared by dissolving Mohr's salt in 0.06 N hydrochloric acid.

Table I. Elemental Analyses of Iron(II) ( $\alpha$ -dioxime) $_2\text{X}_2$

| Compound   | C(%)  |       | H(%)  |       | N(%)  |       |
|--|-------|-------|-------|-------|-------|-------|
|  | Found | Calcd | Found | Calcd | Found | Calcd |
| Fe(II) ( $\text{DgH}$ ) $_2\text{Py}_2$  | 48.61 | 48.66 | 5.41  | 5.44  | 19.55 | 18.92 |
| Fe(II) ( $\text{DgH}$ ) $_2(\text{N-meim})_2$                                    | 42.47 | 42.67 | 6.01  | 5.82  | 25.70 | 24.89 |
| Fe(II) ( $\text{DgH}$ ) $_2(3\text{-CH}_3\text{Py})_2$                           | 48.81 | 49.79 | 6.08  | 5.72  | 18.61 | 18.34 |
| Fe(II) ( $\text{DgH}$ ) $_2(4\text{-CH}_3\text{Py})_2 \cdot 2\text{H}_2\text{O}$ | 49.34 | 49.00 | 6.14  | 6.17  | 17.13 | 17.13 |
| Fe(II) ( $\text{DgH}$ ) $_2(\text{Isoq})_2$                                      | 57.27 | 57.36 | 5.16  | 5.18  | 15.29 | 15.44 |
| Fe(II) ( $\text{DgH}$ ) $_2(4\text{-CNPy})_2 \cdot 2\text{H}_2\text{O}$          | 44.79 | 45.29 | 4.19  | 4.94  | 19.04 | 21.13 |
| Fe(II) ( $\text{DgH}$ ) $_2(4\text{-NH}_2\text{Py})_2 \cdot 2\text{H}_2\text{O}$ | 42.32 | 42.36 | 6.16  | 5.92  | 19.05 | 21.96 |
| Fe(II) ( $\text{DgH}$ ) $_2(3\text{-CHOPy})_2 \cdot 2\text{H}_2\text{O}$         | 44.88 | 44.78 | 5.97  | 5.26  | 13.37 | 15.67 |
| Fe(II) ( $\text{FrH}$ ) $_2\text{Py}_2 \cdot 2\text{H}_2\text{O}$                | 54.16 | 53.74 | 3.67  | 3.91  | 13.06 | 12.55 |
| Fe(II) ( $\text{FrH}$ ) $_2(\text{N-meim})_2$                                    | 50.67 | 51.07 | 3.88  | 3.98  | 17.40 | 17.02 |
| Fe(II) ( $\text{FrH}$ ) $_2(4\text{-CH}_3\text{Py})_2$                           | 55.95 | 56.48 | 3.95  | 4.15  | 12.42 | 12.35 |
| Fe(II) ( $\text{FrH}$ ) $_2(4\text{-CNPy})_2$                                    | 53.72 | 54.71 | 2.73  | 3.16  | 15.72 | 15.96 |
| Fe(II) ( $\text{FrH}$ ) $_2(3\text{-CH}_3\text{Py})_2$                           | 56.30 | 56.48 | 3.97  | 4.15  | 12.37 | 12.35 |

*Procedure of extraction.* To an aqueous solution containing 1.12–11.2  $\mu\text{g}$  of iron in a 30 ml glass-stoppered centrifuge tube, aqueous solutions of 10% hydroxylamine hydrochloride (1 ml) and 1.25 M NaOH (1 ml) were added and then the volume of the mixed solution was adjusted to 10 ml by adding water. The pH value of this aqueous solution was about 7. To the solution, 10 ml of chloroform containing about  $10^{-1}\text{M}$  base and about  $10^{-2}\text{M}$   $\alpha$ -furyldioxime was added and the two phases equilibrated for 30 min and were separated by centrifugation.

Optical absorption measurements were made on a Hitachi 323 automatic recording spectrophotometer. Chloroform and ethanol containing 10% or 0.1 M base were used as solvent. The spectra of the unisolated complexes were measured by dissolving the pyridine complexes to the solvents containing the corresponding bases. The absorbance of iron(II) complexes extracted into chloroform were measured against the corresponding base blanks. The Mössbauer spectra were obtained with a scanning velocity spectrometer in the time mode. The velocity scale was calibrated with metallic iron.

## RESULTS AND DISCUSSION

*Mössbauer Parameter.* The Mössbauer parameters of the iron(II)- $\alpha$ -dioxime complexes are listed in Table II together with the data reported by Dale *et al.*<sup>8)</sup> The isomer shift (I. S.) lies within a range normally found for low-spin complexes.<sup>10)</sup> Obvious

Table II. Mössbauer Parameters of Iron(II) ( $\alpha$ -dioxime)<sub>2</sub>X<sub>2</sub>

| Compound  | Temperature | I. S. | Q. S. |
|---|-------------|-------|-------|
| Fe(II) (DgH) <sub>2</sub> Py <sub>2</sub> <sup>1)</sup>                         | RT          | 0.24  | 1.78  |
|   | ~100K       | 0.26  | 1.73  |
| Fe(II) (DgH) <sub>2</sub> Im <sub>2</sub> <sup>1)</sup>                         | RT          | 0.27  | 1.31  |
|   | ~100K       | 0.31  | 1.29  |
| Fe(II) (DgH) <sub>2</sub> (3-CH <sub>3</sub> Py) <sub>2</sub>                   | RT          | 0.26  | 1.76  |
|   | ~100K       | 0.34  | 1.65  |
| Fe(II) (DgH) <sub>2</sub> (4-CH <sub>3</sub> Py) <sub>2</sub> H <sub>2</sub> O  | RT          | 0.21  | 1.74  |
|   | ~100K       | 0.31  | 1.79  |
| Fe(II) (DgH) <sub>2</sub> (Isoq) <sub>2</sub>                                   | RT          | 0.24  | 1.70  |
|   | ~100K       | 0.31  | 1.75  |
| Fe(II) (DgH) <sub>2</sub> (3-CHOPy) <sub>2</sub> 2H <sub>2</sub> O              | RT          | 0.27  | 1.62  |
|   | ~100K       | 0.31  | 1.63  |
| Fe(II) (DgH) <sub>2</sub> (4-NH <sub>2</sub> Py) <sub>2</sub> 2H <sub>2</sub> O | RT          | 0.21  | 1.59  |
|   | ~100K       | 0.31  | 1.52  |
| Fe(II) (FrH) <sub>2</sub> Py <sub>2</sub> <sup>1)</sup>                         | RT          | 0.19  | 1.90  |
|   | ~100K       | 0.24  | 1.87  |
| Fe(II) (FrH) <sub>2</sub> Im <sub>2</sub> <sup>1)</sup>                         | RT          | 0.21  | 1.44  |
|   | 77K         | 0.25  | 1.41  |
| Fe(II) (CdH) <sub>2</sub> (Buam) <sub>2</sub> <sup>2)</sup>                     | 293K        | 0.22  | 1.83  |
|   | 77K         | 0.31  | 1.85  |

(mm/s)

Im=imidazole, CdH<sub>2</sub>=nioxime, and RT=room temperature.

1) From Ref. 9. 2) From Ref. 8.

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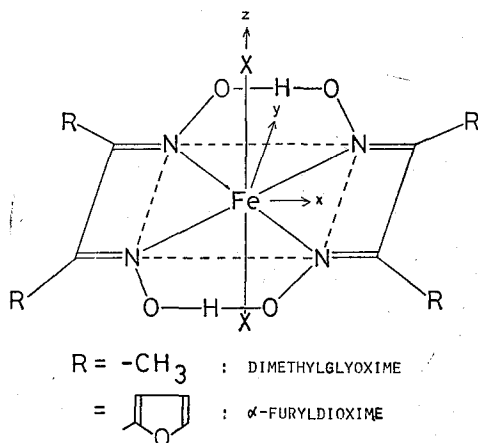


Fig. 1. Structure of the complex  $Fe(II)(\alpha\text{-dioxime})_2X_2$ . (X=base)

Table III. Basis Set Related with the 3d Orbitals for the Symmetry  $D_{2h}$

| $a_g$ :    | 4s        | $3d_{x^2-y^2}$                    | $3d_{x^2-y^2}$ | $\sigma_1(\alpha\text{-dioxime})$ | $\sigma_1(\text{base})$ |
|------------|-----------|-----------------------------------|----------------|-----------------------------------|-------------------------|
| $b_{1g}$ : | $3d_{xy}$ | $\sigma_2(\alpha\text{-dioxime})$ |                |                                   |                         |
| $b_{2g}$ : | $3d_{xz}$ | $\pi_1(\alpha\text{-dioxime})$    |                | $\pi_1(\text{base})$              |                         |
| $b_{3g}$ : | $3d_{yz}$ | $\pi_2(\alpha\text{-dioxime})$    |                |                                   |                         |

axial ligand effect on the I. S. values does not be found. The quadrupole splitting (Q. S.) is relatively large and the change of the Q. S. values due to the substituted groups in the pyridine ring is also little. Since the electronic distribution of a ferrous ion in a strong crystal-field has a cubic symmetry, the electric field-gradient (efg) at the nucleus of Fe in low-spin octahedral complexes may be considered to be that generated by distant charges. Thus such complexes are expected to show a doublet exhibiting a small Q. S. Therefore, the large Q. S. values observed should be mainly generated by the 3d electrons of the iron(II), which is the sum of two contributions; the efg produced by the  $\sigma$ -donated electrons from the ligands and that produced by the  $d\pi$  electrons back-donating to the ligands. According to the X-ray analyses of  $Fe(II)(CdH)_2Im_2$  and  $Fe(II)(DgH)_2Im_2$ , the  $\pi$  rings of imidazole are coplanar and perpendicular to the hydrogen bonds.<sup>1,11</sup> The ground state of the central ion of the complexes in this study is considered to be  $(3d_{x^2-y^2})^2(3d_{xz})^2(3d_{yz})^2$  under the coordinates, as shown in Fig. 1. Assuming that the complexes have approximate  $D_{2h}$  symmetry, the basis set listed in Table III can be chosen. Since the  $3d_{x^2-y^2}$  orbital is considered to be approximately one of nonbonding character,<sup>12</sup> the strong  $\pi$ -interaction between the central ion and the ligands must generate large efg. Therefore, it may be considered to be due to this reason that the Q. S. values of the pyridine complexes are larger than those of the imidazole complexes. On the other hand, the large Q. S. value of the butylamine complex suggests that the strong  $\sigma$ -donation by the axial ligand may increase the efg. It is considered that the two tendencies may give rise to the little dependency of the substituted groups in the pyridine ring on the Q. S. values.

**Absorption Spectra.** The spectra  $Fe(II)(DgH)_2X_2$  and  $Fe(II)(FrH)_2X_2$  are shown in Figs. 2 and 3, respectively. The spectra measured by dissolving the pyridine com-

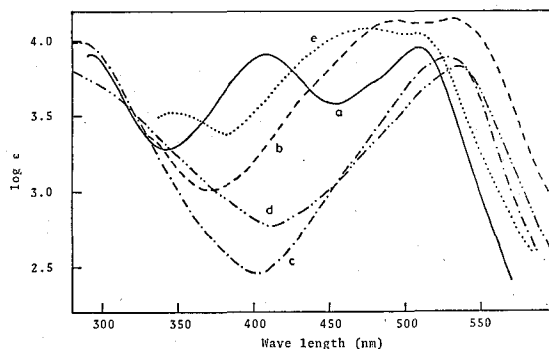


Fig. 2. Absorption spectra of  $\text{Fe(II)(DgH)}_2\text{X}_2$  in chloroform.  
 c:  $\text{Fe(II)(DgH)}_2\text{Py}_2$ , b:  $\text{Fe(II)(DgH)}_2(4\text{-CNPy})_2$ ,  
 c:  $\text{Fe(II)(DgH)}_2(\text{N-meim})_2$ , d:  $\text{Fe(II)(DgH)}_2(\text{Buam})_2$ ,  
 e:  $\text{Fe(II)(DgH)}_2(\text{Isoq})_2$ .

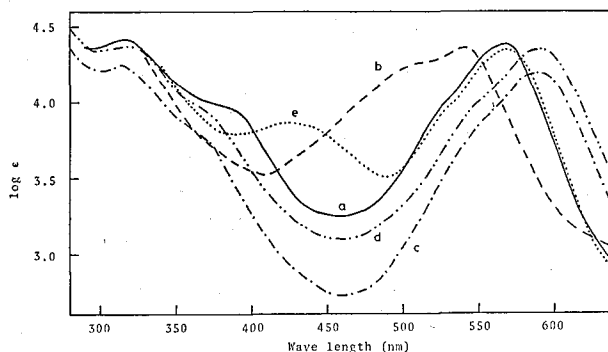
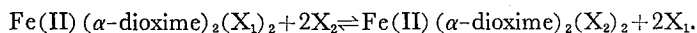


Fig. 3. Absorption spectra of  $\text{Fe(II)(FrH)}_2\text{X}_2$  in chloroform.  
 a:  $\text{Fe(II)(FrH)}_2\text{Py}_2$ , b:  $\text{Fe(II)(FrH)}_2(4\text{-CNPy})_2$ ,  
 c:  $\text{Fe(II)(FrH)}_2(\text{N-meim})_2$ , d:  $\text{Fe(II)(FrH)}_2(\text{Buam})_2$ ,  
 e:  $\text{Fe(II)(FrH)}_2(\text{Isoq})_2$ .

lexes into chloroform containing another base (X) coincide with those of  $\text{Fe(II)(}\alpha\text{-dioxime)}_2\text{X}_2$ , which means that there is a following ligand-exchange equilibrium in solution:



The complexes in this study are considerably stable in solution in the presence of excess of the bases (especially the  $\alpha$ -furyldioxime complexes). They are, however, oxidized easily in the presence of small content of the bases. The complexes are rapidly oxidized in the presence of  $\alpha$ -picoline, 2, 6-lutidine and piperidine.

The bands at about 510 nm in the spectra of  $\text{Fe(II)(DgH)}_2\text{X}_2$  and those at about 560 nm in the spectra of  $\text{Fe(II)(FrH)}_2\text{X}_2$  are assigned to the  $d\pi \rightarrow \pi^*(\alpha\text{-dioxime})$  CT bands<sup>5)</sup>. These bands shift to a longer wave length with the increase in the basicity of the bases. On the other hand, the  $d\pi \rightarrow \pi^*(\text{base})$  CT bands of  $\text{Fe(II)(DgH)}_2\text{X}_2$  shift to a longer wave length in the order: pyridine (411nm) > isoquinoline (480nm) > 4-cyanopyridine (532nm). The  $\alpha$ -furyldioxime complexes also show the same tendency. In the complexes of butylamine and N-methylimidazole which are not or poor  $\pi$ -acceptors,

# Characterization of Fe(II) Complexes with $\alpha$ -Dioximes

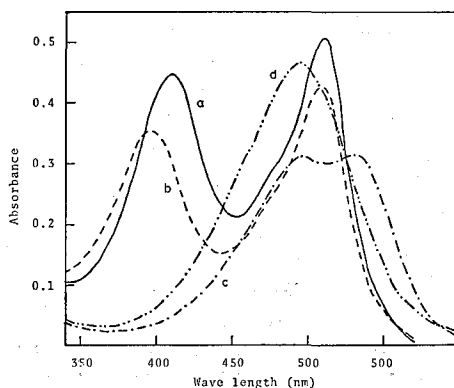


Fig. 4. Solvent dependency of absorption spectra of Fe(II) (DgH)<sub>2</sub>X<sub>2</sub>.

- a: Fe(II) (DgH)<sub>2</sub>Py<sub>2</sub> in chloroform,
- b: Fe(II) (DgH)<sub>2</sub>Py<sub>2</sub> in ethanol,
- c: Fe(II) (DgH)<sub>2</sub>(4-CNPy)<sub>2</sub> in chloroform,
- d: Fe(II) (DgH)<sub>2</sub>(4-CNPy)<sub>2</sub> in ethanol.

the  $d\pi \rightarrow \pi^*(\text{base})$  CT bands are not observed.

The  $d\pi \rightarrow \pi^*(\text{base})$  CT bands of Fe(II) (DgH)<sub>2</sub>X<sub>2</sub> shift to a longer wave length with a change of solvent from ethanol to chloroform, as shown in Fig. 4. The shift in Fe(II) (DgH)<sub>2</sub>(4-CNPy)<sub>2</sub> is especially large (2,760 cm<sup>-1</sup>). Such effects are not found on the absorption bands of Fe(II) (FrH)<sub>2</sub>X<sub>2</sub> and the  $d\pi \rightarrow \pi^*(\text{dimethylglyoxime})$  CT bands. The large solvent shift of the  $d\pi \rightarrow \pi^*(\text{base})$  CT bands does not result from dissociation of Fe(II) (DgH)<sub>2</sub>X<sub>2</sub>, for the band positions are unaltered by the content of the bases. The solvent dependency is opposite to that produced by the change of the dielectric

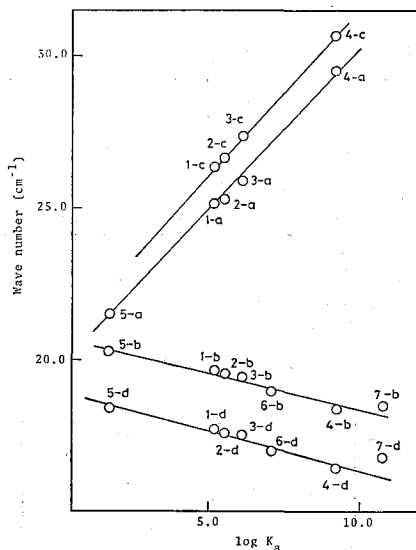


Fig. 5. Plots of absorption maxima of iron(II) complexes in ethanol against  $pK_a$  values of the conjugated acids of free bases.

- a:  $d\pi \rightarrow \pi^*(\text{base})$  band of Fe(II) (DgH)<sub>2</sub>X<sub>2</sub>,
  - b:  $d\pi \rightarrow \pi^*(\text{dimethylglyoxime})$  band of Fe(II) (DgH)<sub>2</sub>X<sub>2</sub>,
  - c:  $d\pi \rightarrow \pi^*(\text{base})$  band of Fe(II) (FrH)<sub>2</sub>X<sub>2</sub>,
  - d:  $d\pi \rightarrow \pi^*(\alpha\text{-furyldioxime})$  band of Fe(II) (FrH)<sub>2</sub>X<sub>2</sub>.
- 1: pyridine, 2:  $\beta$ -picoline, 3:  $\gamma$ -picoline, 4: 4-aminopyridine,  
5: 4-cyanopyridine, 6: N-methylimidazole, 7: butylamine.

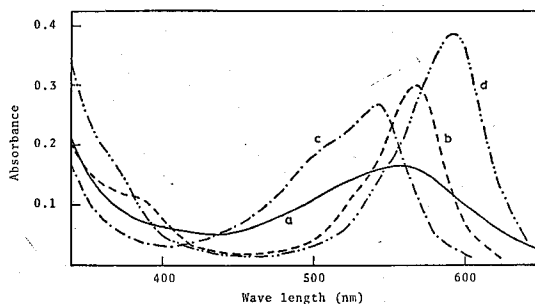


Fig. 6. Absorption spectra of iron(II) complexes extracted into chloroform. Measured against corresponding base blanks in 10-mm cells. Iron(II) concentration:  $2.014 \times 10^{-5} \text{M}$ ,  $\alpha$ -furyldioxime concentration:  $0.972 \times 10^{-2} \text{M}$ . a: no base, b: pyridine ( $0.985 \times 10^{-1} \text{M}$ ), c: 4-cyanopyridine ( $1.42 \times 10^{-1} \text{M}$ ), d: butylamine ( $0.983 \times 10^{-1} \text{M}$ ).

constant of the solvents, which is considered to be related to stability of the excited charge-transfer structure of  $\text{Fe(II)(DgH)}_2\text{X}_2$ . Thus the most likely cause is probably a considerable geometrical change in the complexes; the rotational distortion of the bases about the z axis, as pointed out by Sanders and Day in connection with a solvent effect on the  $d\pi \rightarrow \pi^*$ (pyridine) CT bands of  $\text{Fe(II)(CdH)}_2\text{Py}_2$ .<sup>6)</sup> There are linear relationships between the wave numbers of the CT bands and the basicities of the free bases in this study (Fig. 5), as found by Yamano *et al.* in the dimethylglyoxime complexes.<sup>7)</sup> Figure 5 suggests that the excited charge-transfer structure of the complexes is further stabilized with the increase of the  $\pi$ -acceptor property of the bases and that the  $d\pi$  orbitals ( $3d_{xz}$ ,  $3d_{yz}$ ) of the central metal ion are unstabilized with the axial ligation of the bases.

*Possibility of an Application of  $\alpha$ -Furyldioxime to Extraction and Determination of Iron(II).* The  $\alpha$ -dioxime complexes exhibit large molar extinction coefficients (about  $1-2 \times 10^4 \text{ dm}^3/(\text{mol cm})$ ), as shown in Figs. 2 and 3. Though the spectra of the dimethylglyoxime complexes change very slowly in the presence of excess of the bases, those of the  $\alpha$ -furyldioxime complexes unalter for several hours even in the addition of  $10^{-3} \text{M}$  of the bases. These results suggest that  $\alpha$ -furyldioxime may be effective on a highly sensitive determination of iron(II). Figure 6 shows the spectra of the iron(II) complexes extracted into chloroform. The spectrum in absence of the bases is considered

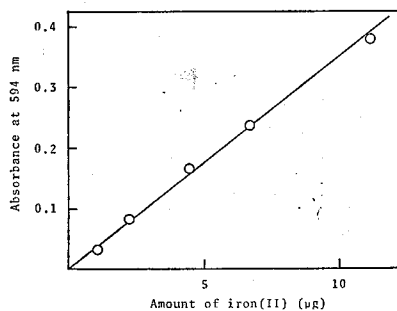


Fig. 7. Calibration curve of  $\text{Fe(II)(FrH)}_2(\text{Buam})_2$  extracted into chloroform.



to be due to iron(II) complex containing hydroxylamine. The other spectra coincide with those of the complexes with the corresponding bases, which means that the species extracted are in the form of  $\text{Fe(II)(FrH)}_2\text{X}_2$ . Figure 7 shows the plots of the absorbance at 594 nm in the butylamine system against the amount of iron(II). A straight line passing through the origin is obtained in the range 1.12–11.2  $\mu\text{g}$  and the molar extinction coefficient value estimated is 19,800  $\text{dm}^3/(\text{mol cm})$ , which compares with those in the methods using bathophenanthroline and 2,4,6-tripyridyl-s-triazine for extraction and determination of iron(II).<sup>13,14)</sup>

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